Electronic Supplementary Information

Synthesis and Characterization of Cyano and Isocyano Complexes of Bis(dithiolato) Molybdenum Using Me_3SiCN: A Route to A Cyanide-Bridged Multimer to A Monomer.

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1. Infrared spectra

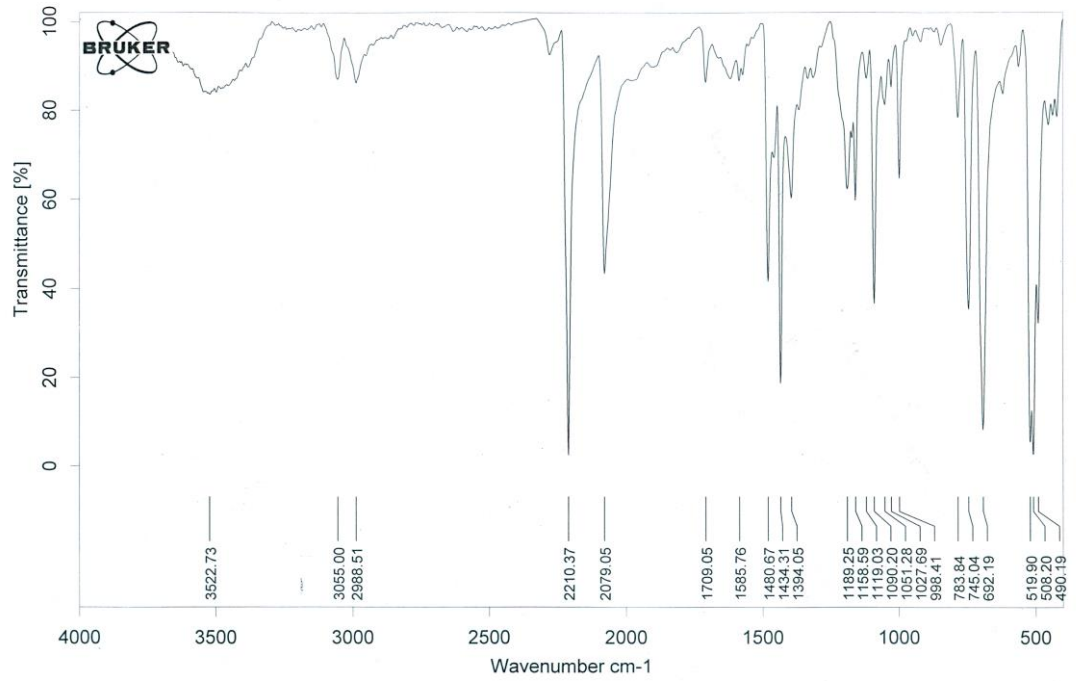


Figure S1. IR spectrum of $[Et_4N][(mnt)_2(PPh_3)Mo(\mu\text{-}CN)Mo(PPh_3)(mnt)_2].2CH_2Cl_2.C_6H_6.H_2O$ **(3)**

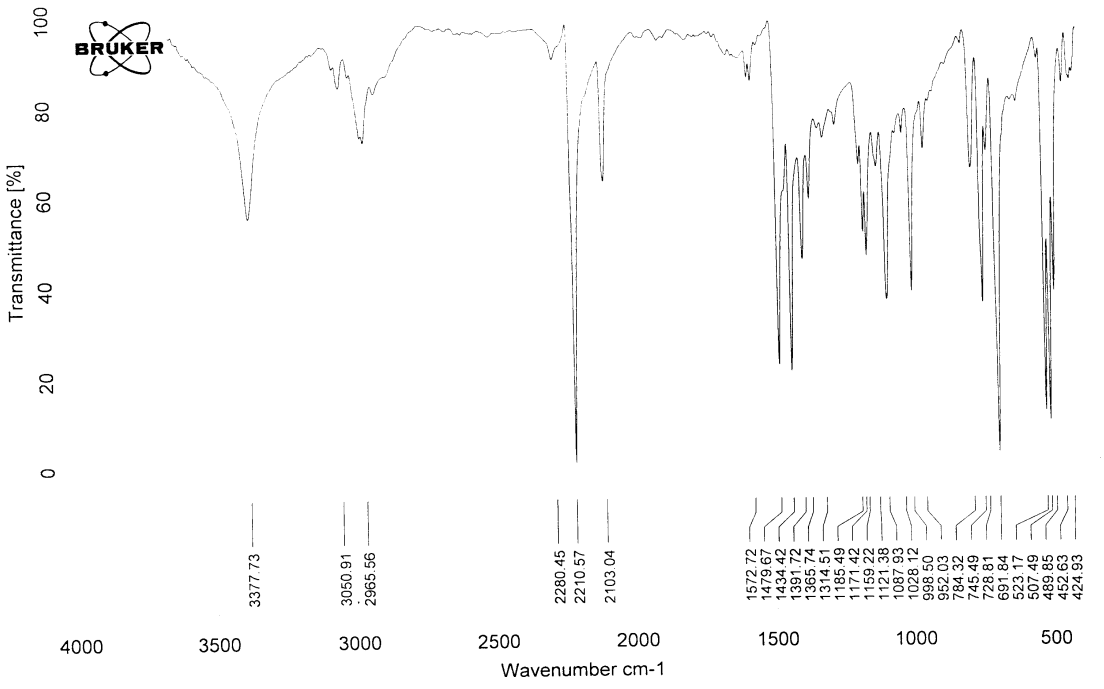


Figure S2. IR spectrum of$[Et_4N][Mo(PPh_3)(CN)(mnt)_2].CH_2Cl_2$ **(4)**

2. ^{31}P NMR

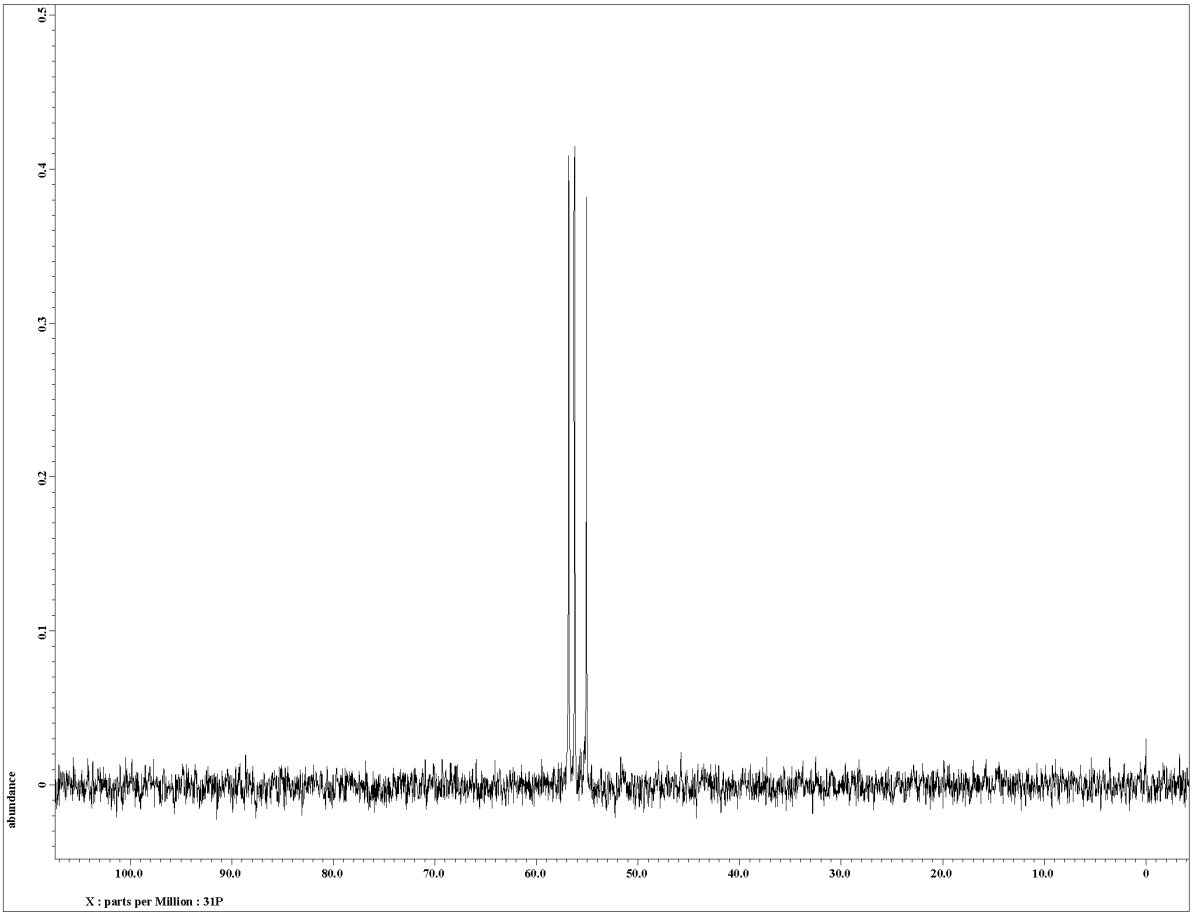


Figure S3. ^{31}P NMR of $[Et_4N][(mnt)_2(PPh_3)Mo(\mu\text{-}CN)Mo(PPh_3)(mnt)_2].2CH_2Cl_2.C_6H_6.H_2O$ (**3**)

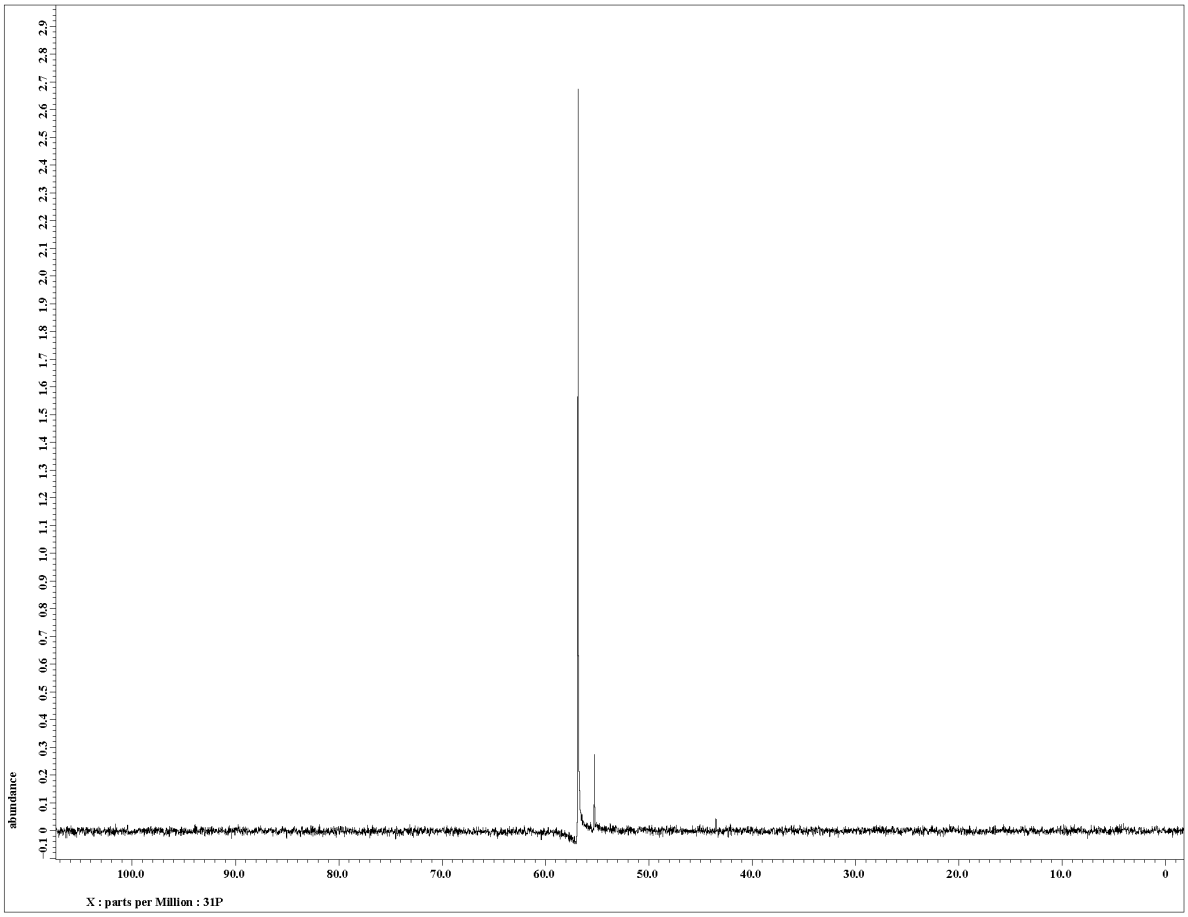


Figure S4. ^{31}P NMR of $[Et_4N][Mo(PPh_3)(CN)(mnt)_2].CH_2Cl_2$ (**4**)

3. Magnetism of the Complex 4:

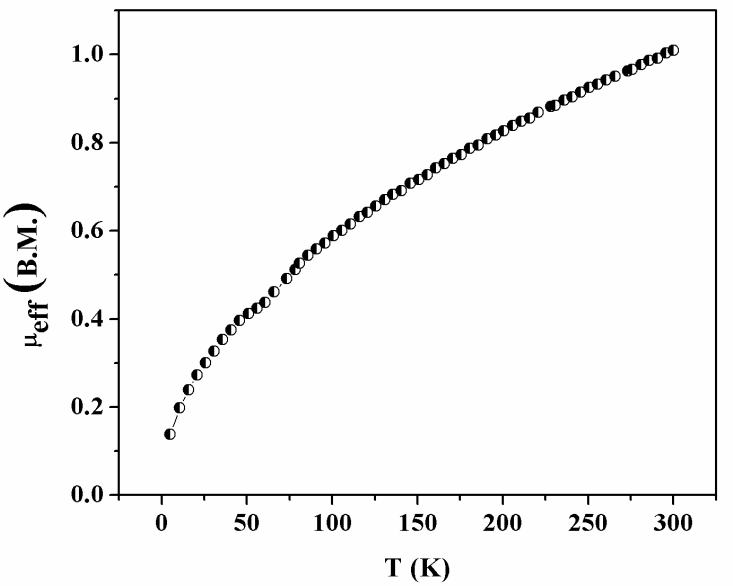


Figure S5: Magnetic moment of the complex **4** as measured under an applied field of 1000 G using a SQUID magnetometer.

4. Electrochemistry of the Complex 5:

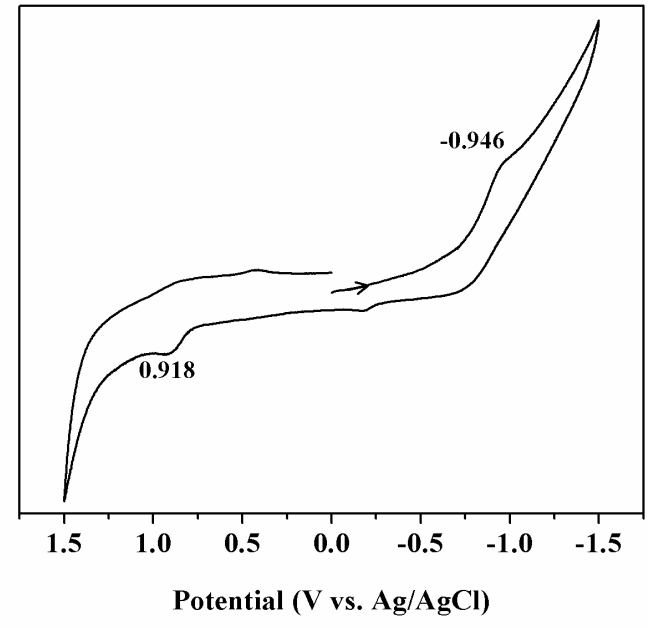
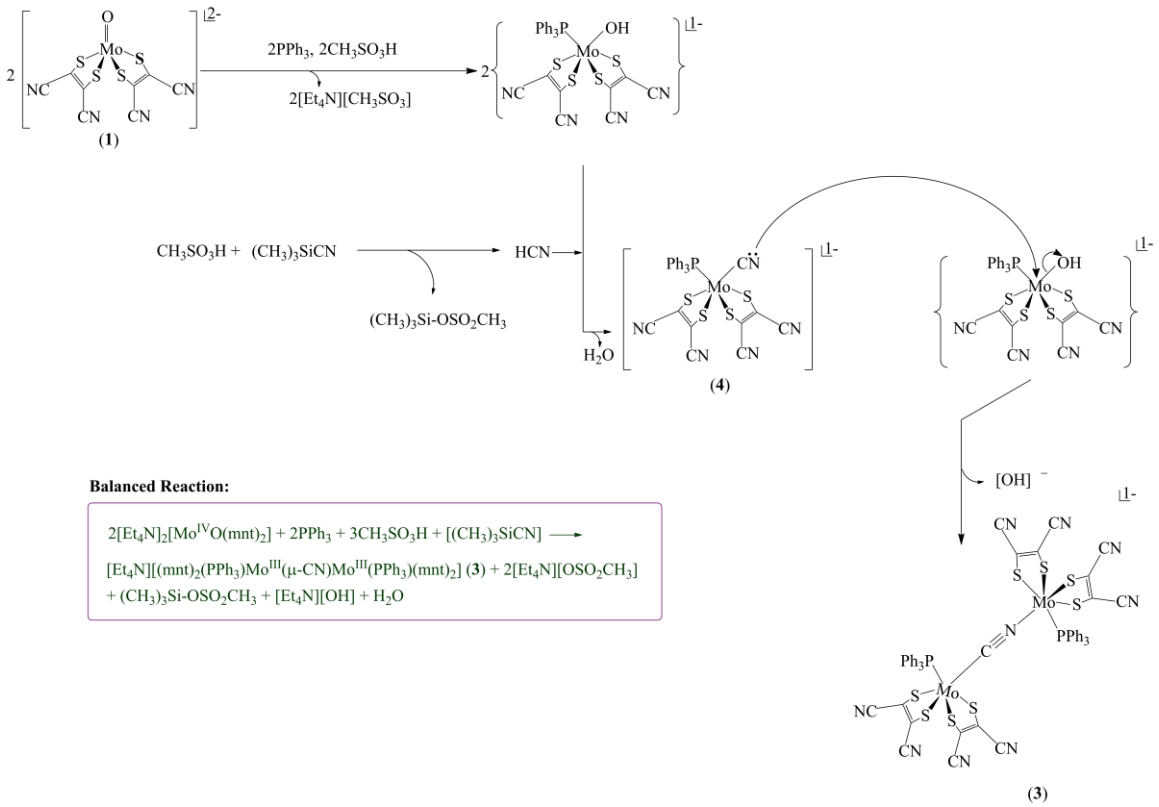
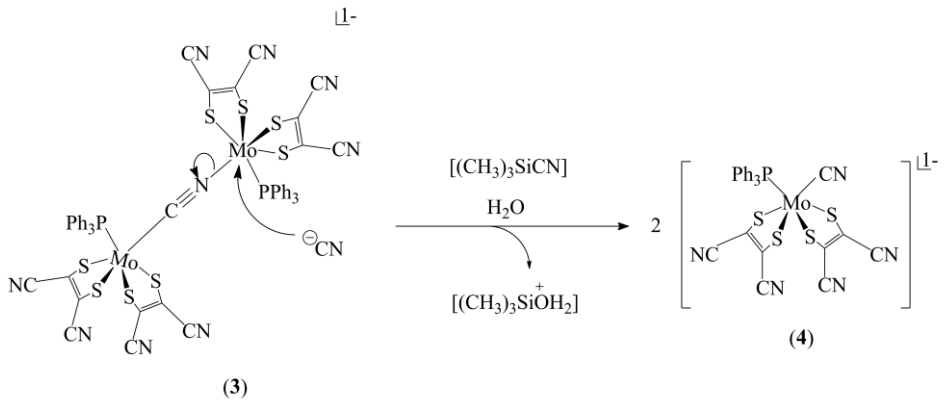


Figure S6: Cyclic voltammetric traces; reductive scan for the complex **5** in dichloromethane.

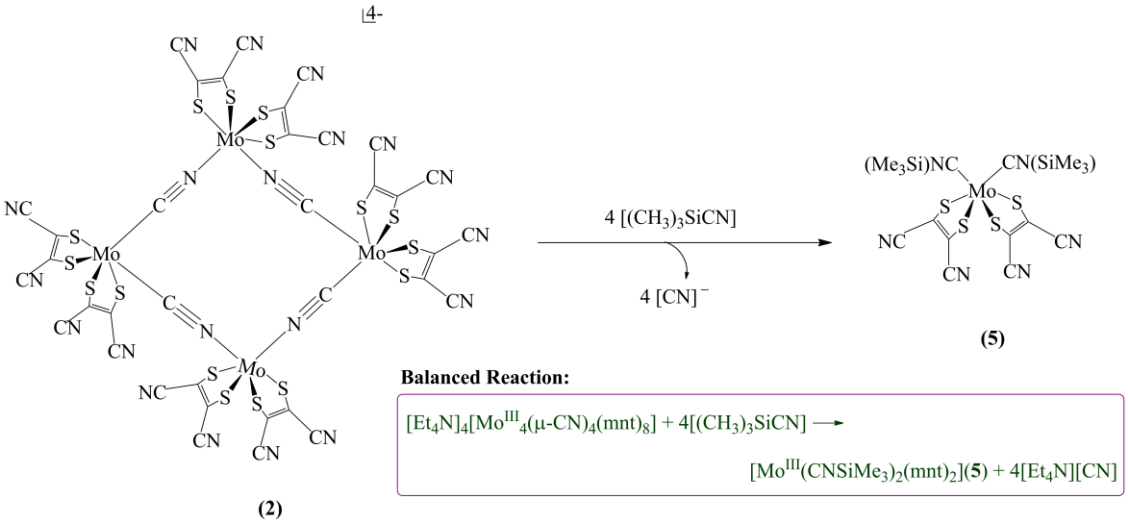
5. Tentative Mechanisms for the Formation of the Complexes 3-5



Scheme S1. A tentative mechanism for the formation of the complex (**3**).



Scheme S2. A tentative mechanism for the formation of the complex (**4**).



Scheme S3. A tentative mechanism for the formation of the complex (**5**).

6. TD-DFT Results

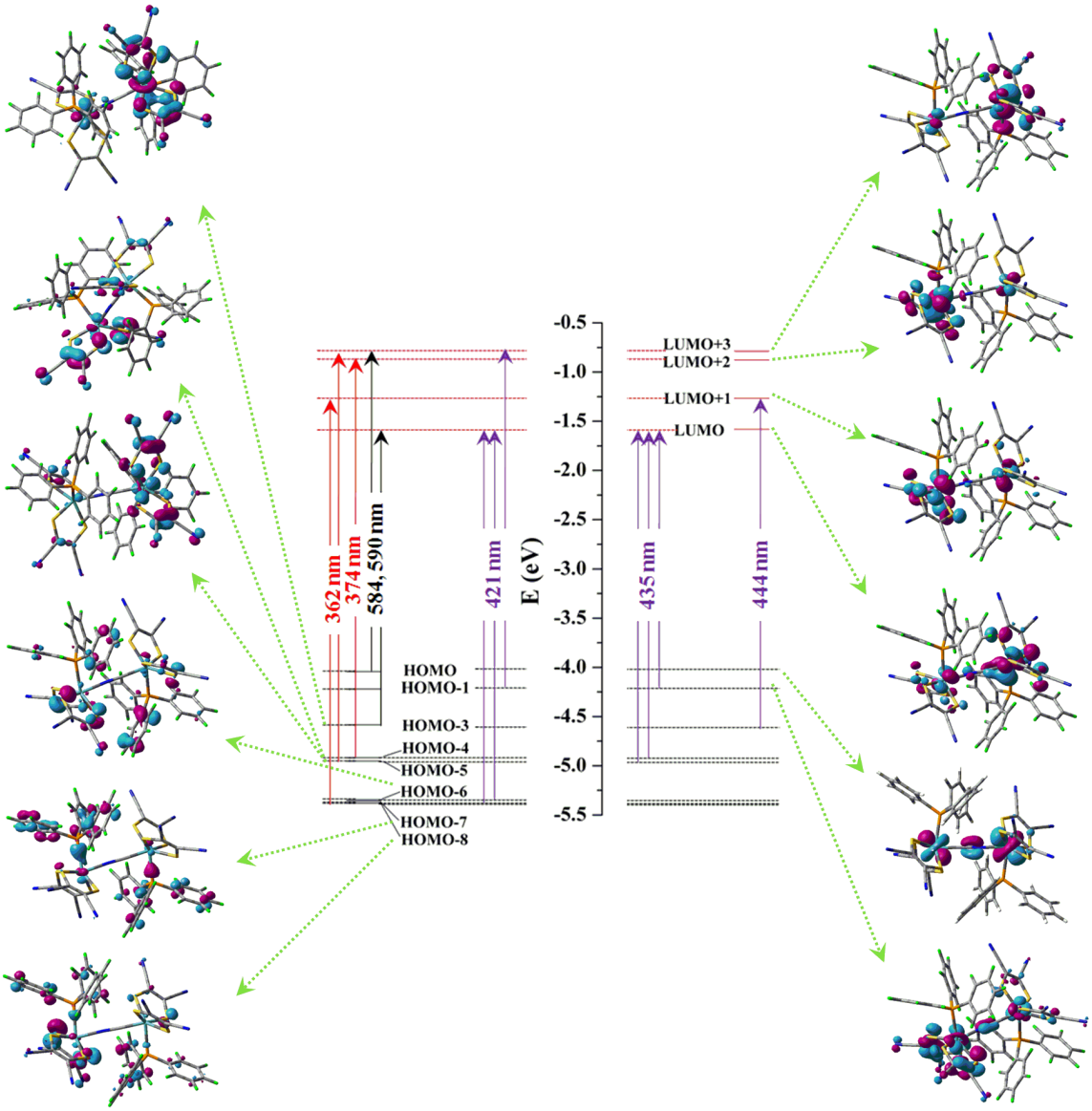


Figure S7. Kohn–Sham orbitals of the complex $[Et_4N][(mnt)_2(PPh_3)Mo(\mu\text{-}CN)Mo(PPh_3)(mnt)_2].2CH_2Cl_2.C_6H_6.H_2O$ **(3)** involved in TD-DFT vertical transitions.

Table S1. TD-DFT calculations based on ground state geometry of the complex $[Et_4N][(mnt)_2(PPh_3)Mo(\mu\text{-}CN)Mo(PPh_3)(mnt)_2].2CH_2Cl_2.C_6H_6.H_2O$ **(3)**.

State	Energy (eV)	Main excitation(%)[a]	Assignment(f)[b]	TD-DFT λ_{max} (nm)[c]	Exp. λ_{max} (nm)
S_4	2.0986	H-1→L(46) H→L+3(17)	ML′MLCT(0.0873)	590	549
S_5	2.1228	H-1→L(27) H→L+3(31)	ML′MLCT(0.0572)	584	
S_{14}	2.7924	H-3→L+1(82)	ML′MLCT(0.0248)	444	409
S_{16}	2.8480	H-5→L(13) H-4→L(40) H-1→L+3(14)	LMCT ML′MCT (0.0678)	435	
S_{17}	2.9445	H-7→L(11) H-6→L(23) H-1→L+3(15)	LMCT ML′MCT (0.0698)	421	
S_{40}	3.3134	H-4→L+2(74)	L′MLCT(0.0427)	374	339
S_{49}	3.4205	H-8→L+1(16) H-5→L+3(32)	L′MLCT ML′MCT(0.0652)	362	

[a] H and L denote HOMO and LUMO, respectively. [b] The values between in parentheses indicate oscillator strength, f. [c] In solution phase (dichloromethane).

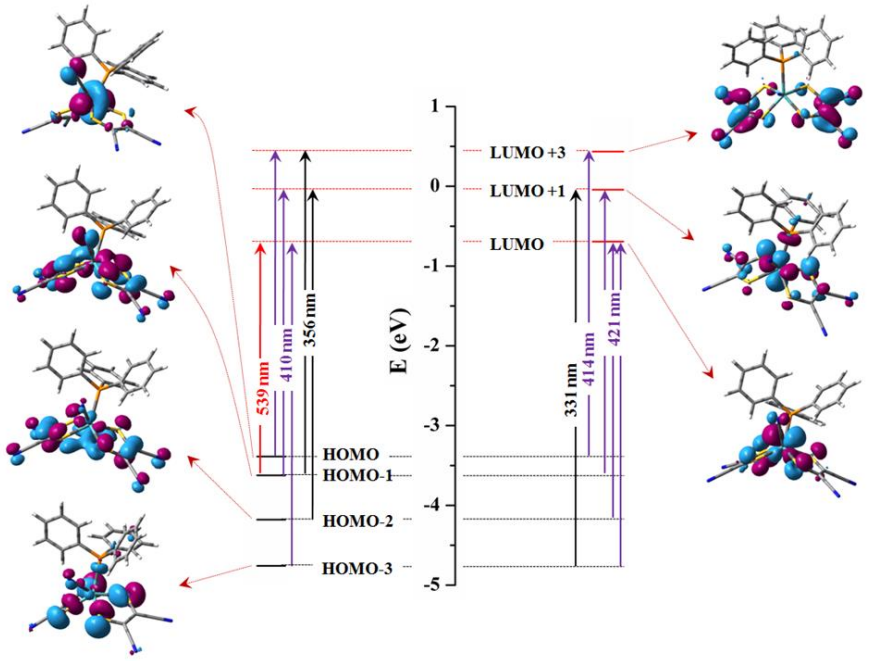


Figure S8. Kohn–Sham orbitals of the complex $[Et_4N][Mo(PPh_3)(CN)(mnt)_2].CH_2Cl_2$ **(4)** involved in TD-DFT vertical transitions.

Table S2. TD-DFT calculations based on ground state geometry of the complex $[Et_4N][Mo(PPh_3)(CN)(mnt)_2].CH_2Cl_2$ **(4)**

State	Energy (eV)	Main excitation(%)[a]	Assignment(f)[b]	TD-DFT λ_{max} (nm)[c]	Exp. λ_{max} (nm)
S_3	2.2993	H-1→L(86)	ML′MLCT (0.0452)	539	504
S_6	2.9434	H-3→L(30) H-2→L(43) H-1→L+1(14)	L′MLCT ML′MLCT (0.0296)	421	405
S_7	2.9884	H→L+3(72)	MLCT (0.0352)	414	
S_8	3.0205	H-3→L(34) H-1→L+1(19) H→L+3(21)	L′MLCT ML′MLCT MLCT(0.1326)	410	
S_{15}	3.4747	H-2→L+1(61) H-1→L+3(11)	ML′MLCT ML′LCT (0.0518)	356	333
S_{22}	3.7421	H-3→L+1(56)	LMCT(0.0645)	331	

[a] H and L denote HOMO and LUMO, respectively. [b] The values between in parentheses indicate oscillator strength, f. [c] In solution phase (dichloromethane).

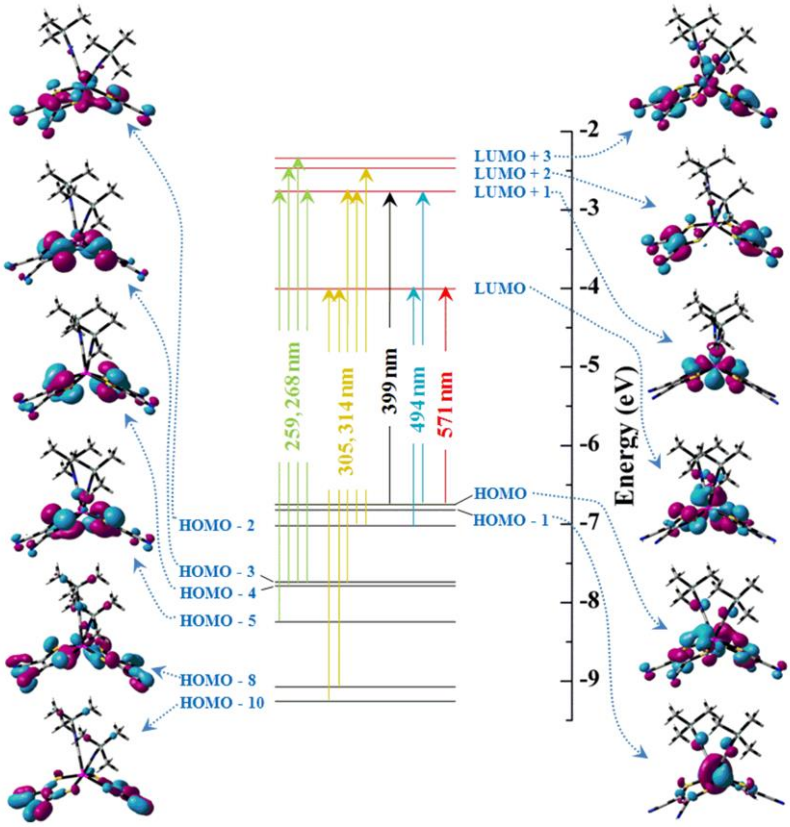


Figure S9. Kohn–Sham orbitals of the complex $[Mo^{IV}(CNSiMe_3)_2(mnt)_2]$ (**5**) involved in TD-DFT vertical transitions.

Table S3. TD-DFT calculations based on optimized geometry of the complex $[Mo(CNSiMe_3)_2(mnt)_2]$ (**5**)

State	Energy (eV)	Main excitation(%)[a]	Assignment(f)[b]	TD-DFT λ_{max} (nm)[c]	Exp. λ_{max} (nm)
2	2.1684	H→L(95)	ML′MLCT (0.0634)	571	565
3	2.5059	H-2→ L (87) H→ L+1(10)	ML′MLCT (0.1246)	494	513
6	3.1011	H→L+1(86)	ML′MLCT (0.1881)	399	395
16	3.9376	H-3→L+1(31) H-2→L+2(64)	L′MLCT ML′LCT (0.0329)	314	330
17	4.0521	H-10→L(64) H-8→L(16) H-2→L+1(11)	L′MLCT ML′MLCT (0.0396)	305	
31	4.6224	H-4→L+2(63) H-3→L+3(25)	LLCT (0.3582)	268	262
33	4.7823	H-5→L+1(42) H-3→L+1(20)	L′MLCT (0.1753)	259	

[a] H and L denote HOMO and LUMO, respectively. [b] The values between in parentheses indicate oscillator strength, f. [c] In solution phase (dichloromethane).

7. Optimized Coordinates of $[(mnt)_2(PPh_3)Mo(\mu\text{-}CN)Mo(PPh_3)(mnt)_2]^{1-}$

C	2.38365600	2.49744700	4.81725900
C	2.75965200	1.94204900	3.55760000
C	4.02318400	1.45487100	3.30906000
C	5.05284100	1.46074100	4.29588200
C	4.42098000	3.45392700	-3.35523200
C	3.57089500	2.96218300	-2.32112700
C	2.33929300	3.51472400	-2.05271600
C	1.82182400	4.61838800	-2.79393800
C	2.62687600	-1.80633800	-2.09670000
C	1.74462400	-0.98823200	-2.81557000
H	1.38271000	-0.06659000	-2.37423500
C	1.33391400	-1.34736300	-4.10106700
H	0.64787700	-0.70394800	-4.64504600
C	1.79485000	-2.52770400	-4.68340500
H	1.45860900	-2.81545300	-5.67499700
C	2.68798500	-3.34139600	-3.98256000
H	3.05798300	-4.25857300	-4.43225600
C	3.10834400	-2.98122000	-2.70312400
H	3.81895300	-3.61284600	-2.17913300
C	4.95366700	-1.77590500	-0.40369200
C	5.55926600	-2.40888100	0.69226100
H	4.96481300	-2.69707400	1.55213700
C	6.92832400	-2.68050500	0.68577600
H	7.37926100	-3.17264900	1.54321100
C	7.71198600	-2.32180900	-0.41139300
H	8.77833700	-2.53168100	-0.41324700
C	7.11901000	-1.69129900	-1.50655400
H	7.71920100	-1.40681700	-2.36650800
C	5.75084100	-1.41893400	-1.50494100
H	5.30550100	-0.93395800	-2.36642400
C	2.41585500	-2.59875100	0.75238500
C	2.40048300	-2.32984800	2.13175100
H	2.74801900	-1.37091000	2.49979300
C	1.93421600	-3.28463800	3.03602800
H	1.92584200	-3.05761100	4.09829900
C	1.45914200	-4.51382900	2.57692800
H	1.07568500	-5.24666400	3.28112100
C	1.44713900	-4.77929800	1.20724200
H	1.05571100	-5.72281700	0.83709100
C	1.92081700	-3.83124500	0.29853300
H	1.88610600	-4.05261300	-0.76135000
C	-2.75765000	-2.80030100	2.92910900
C	-2.38375700	-3.67156600	3.99600200
C	-4.02545700	-2.28040400	2.80524600
C	-5.06489600	-2.55599300	3.74066400
C	-2.33145300	-2.90546700	-2.84234500
C	-1.81769900	-3.80163600	-3.82668700
C	-3.56454300	-2.30951300	-2.96659800
C	-4.42167800	-2.53670000	-4.08221900
C	-4.95875600	1.83302800	0.05169700
C	-5.57006800	2.17635700	1.26699100
H	-4.97853800	2.25015600	2.17286300
C	-6.94093300	2.43295700	1.32266200
H	-7.39642500	2.69845400	2.27281500

C	-7.72062300	2.34745400	0.16883500
H	-8.78838900	2.54472600	0.21490500
C	-7.12185000	2.00626400	-1.04507600
H	-7.71894400	1.93576200	-1.95015600
C	-5.75193700	1.75011900	-1.10567800
H	-5.30237100	1.49227700	-2.05814400
C	-2.62384900	2.29400000	-1.57006000
C	-3.11243500	3.57790800	-1.87299200
H	-3.83231700	4.05477900	-1.21490000
C	-2.68669800	4.24485400	-3.02082000
H	-3.06230400	5.24155000	-3.23498300
C	-1.78064700	3.63495100	-3.89138500
H	-1.43886700	4.16037800	-4.77801500
C	-1.31244500	2.35101400	-3.61258100
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C	-1.46214900	4.34966600	2.37141800
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C	-1.47633100	3.75102600	3.63156000
H	-1.09707200	4.28619700	4.49743900
C	-1.95070600	2.44568200	3.76891300
H	-1.94514200	1.96184200	4.74149500
C	-2.41465400	1.74574400	2.65452200
H	-2.76319800	0.72538100	2.77220500
C	0.55238600	0.22951400	0.18818000
N	2.03730500	2.95834100	5.82955700
N	5.90886100	1.44727100	5.08596900
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N	-1.37326600	-4.52124900	-4.62788500
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N	-0.54278600	-0.18899500	0.12464000
P	3.15214000	-1.34427500	-0.39124900
P	-3.15626200	1.42099200	-0.03750400
S	1.53971300	1.91797100	2.31372800
S	4.42327000	0.80003100	1.74084300
S	4.15875000	1.62325700	-1.36948300
S	1.34326000	2.87542500	-0.77216500
S	-1.32652000	-2.58025300	-1.45555100
S	-4.14463200	-1.23814200	-1.71208700
S	-1.52742900	-2.42109900	1.75670400
S	-4.41534400	-1.23729700	1.45562000
Mo	2.51689900	1.08473500	0.30164400
Mo	-2.50645400	-1.10285500	0.02268700

8. Optimized Coordinates of $[Mo(PPh_3)(CN)(mnt)_2]^{1-}$

C	-4.68227000	-2.70487500	-0.56135600
C	-3.46476300	-2.05030300	-0.20591100
C	-3.32924700	-1.35271200	0.97304100
C	-4.39248700	-1.22763600	1.91436300
C	3.11385800	-4.39148800	-0.54308000
C	2.28145900	-3.28459800	-0.19809500
C	2.45677900	-2.57897000	0.97129300
C	3.48421900	-2.89377900	1.90839300
C	-0.10148300	-0.34621200	-2.38596100
C	-3.12907200	4.36406600	-1.37204500
H	-3.93334000	5.03296000	-1.66798600
C	-2.14406700	4.80192600	-0.48496300
H	-2.17572700	5.81251500	-0.08562400
C	-1.11656000	3.94033400	-0.09889500
H	-0.36733000	4.28883300	0.60448000
C	-1.05680200	2.62732600	-0.59905700
C	-2.05195400	2.19735900	-1.48964300
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C	-3.07852800	3.06273200	-1.87221700
H	-3.84041200	2.71090100	-2.56212600
C	1.86876800	3.29111000	-1.66402600
H	1.05700100	4.00025700	-1.54513000
C	3.00103600	3.66420300	-2.38925200
H	3.05764700	4.66115000	-2.81895900
C	4.04985100	2.76147700	-2.57014100
H	4.92918300	3.05238200	-3.13923100
C	3.95859800	1.47926200	-2.02743000
H	4.76241400	0.76301500	-2.17352500
C	2.82430500	1.10045300	-1.30876700
H	2.75316000	0.09396300	-0.91099900
C	1.77095500	2.00613200	-1.11140000
C	2.07436100	2.28210400	1.97965500
H	2.87270000	2.14137800	1.25916300
C	2.38953300	2.66845200	3.28356000
H	3.42948100	2.82109800	3.55922400
C	1.37831300	2.85199900	4.22686400
H	1.62535900	3.14937000	5.24281900
C	0.04740200	2.64554600	3.85978700
H	-0.74886800	2.77994300	4.58692200
C	-0.27149000	2.25798600	2.55830000
H	-1.31041000	2.10006100	2.29149100
C	0.73990900	2.07555400	1.59912800
N	-5.66656100	-3.24357000	-0.87523700
N	-5.26319900	-1.12128500	2.68177500
N	3.78611300	-5.29305300	-0.84793800
N	4.32129100	-3.12079200	2.68717900
N	-0.04242100	0.06696100	-3.48111900
P	0.30932500	1.48203200	-0.10280000
S	-2.13639600	-2.16547900	-1.33080500
S	-1.80624600	-0.59429800	1.37698600
S	1.02087000	-2.84852600	-1.32386200
S	1.39733300	-1.24439800	1.36486800
Mo	-0.23831500	-1.04026700	-0.38342900

9. Optimized Coordinates of [Mo(CNSiMe$_3$)$_2$(mnt)$_2$]

C	-2.66441400	-1.68813800	-3.91923300
C	-2.08126600	-0.86545100	-2.90964300
C	-2.07985100	0.51170400	-2.99289400
C	-2.66127700	1.20824400	-4.09417000
C	0.98971500	1.37162100	-0.07720700
C	4.08734300	3.11912000	-1.75705700
H	4.58466600	2.14344600	-1.72273400
H	4.86194000	3.88459400	-1.88822900
H	3.44377300	3.14107000	-2.64341300
C	2.14018800	5.05398800	-0.24943800
H	1.49247800	5.09831400	-1.13192700
H	2.82394300	5.91073100	-0.29190700
H	1.50966800	5.17251800	0.63862900
C	4.12691400	3.25447400	1.37030500
H	3.50689000	3.35803800	2.26758600
H	4.90619900	4.02523900	1.41257700
H	4.62122300	2.27748600	1.40978200
N	-3.12352900	-2.38356000	-4.73214400
N	-3.11878600	1.80203700	-4.98485700
N	1.87454600	2.14496000	-0.12047100
Si	3.10420400	3.44688200	-0.19194200
S	-1.36189400	-1.67235400	-1.54989300
S	-1.35902500	1.47489800	-1.73959000
Mo	-0.58699300	-0.00011300	0.00007700
C	-2.66396300	1.68676600	3.92012000
C	-2.08063100	0.86442400	2.91035100
C	-2.07820900	-0.51272600	2.99372400
C	-2.65867300	-1.20958200	4.09530400
C	0.99051500	-1.37098900	0.07669600
C	4.08613200	-3.12019800	1.75826600
H	4.58286400	-2.14412400	1.72691500
H	4.86101500	-3.88544100	1.88911900
H	3.44104400	-3.14450800	2.64345500
C	2.14249200	-5.05301400	0.24367800
H	1.49313100	-5.09908300	1.12487000
H	2.82654200	-5.90952600	0.28603800
H	1.51370600	-5.17034700	-0.64577000
C	4.13126100	-3.24956000	-1.36928000
H	3.51285400	-3.35145500	-2.26786600
H	4.91082400	-4.02003100	-1.41173100
H	4.62538000	-2.27236300	-1.40588600
N	-3.12325500	2.38191600	4.73316400
N	-3.11538300	-1.80363000	4.98623200
N	1.87574500	-2.14389100	0.11963600
Si	3.10588900	-3.44537300	0.19079900
S	-1.36239100	1.67172600	1.55025000
S	-1.35723900	-1.47551100	1.74018400

10. Energy of the complex [Mo(CNSiMe$_3$)$_2$(mnt)$_2$] (5) and [Mo(NCSiMe$_3$)$_2$(mnt)$_2$]

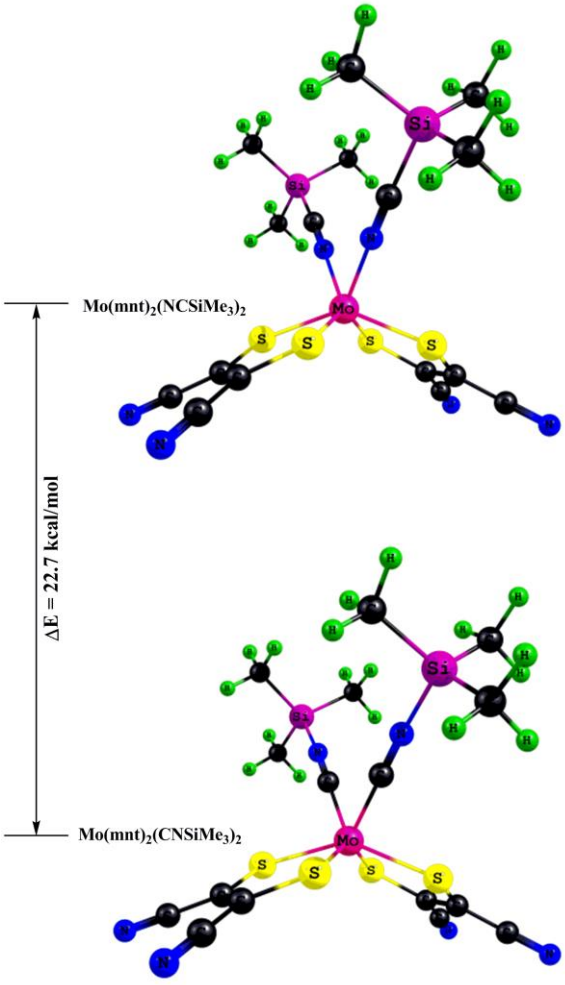

Figure S10. Energy of the complex [Mo(CNSiMe$_3$)$_2$(mnt)$_2$] (**5**) and [Mo(NCSiMe$_3$)$_2$(mnt)$_2$].